

## PATENT ABSTRACTS OF JAPAN

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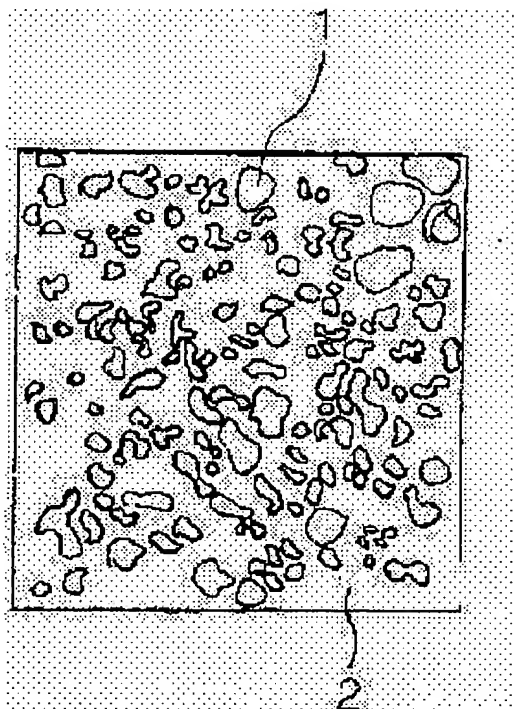
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### (54) COPPER SHEET WITH PATINA-COLORED DOTTED PATTERN AND TREATMENT METHOD THEREFOR

#### (57)Abstract:

PROBLEM TO BE SOLVED: To form a patina-colored dotted pattern of which coloring treatment can chemically and easily performed to a large and thin copper or copper alloy sheet at ordinary temperature so as to prevent thermal strain and thermal deformation, has excellent adhesion and durability of a colored film, and imparts a noble feeling close to that in a natural patina color, and a steel sheet obtained in this way.

SOLUTION: The patina-colored dotted pattern is chemically formed on the surface of a copper sheet. In this coloring method, the surface of the copper sheet is subjected to primary blackening treatment with an acidic aqueous solution containing selenium, and is subjected to base patina treatment with an acidic aqueous solution containing carbonate or/and chloride. After that, the copper sheet is subjected to acid cleaning, and is subjected to secondary blackening treatment with the acidic aqueous solution containing selenium. After that, the surface of the copper sheet is sprayed with an acid aqueous solution containing carbonate or/and chloride to form a patina-colored dotted pattern. If required, after the spraying, a patting is performed thereto with a cloth or the like.



## LEGAL STATUS

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CLAIMS

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[Claim(s)]

[Claim 1] The copper plate of the copper rust colored spot point pattern characterized by processing the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, processing after that in a carbonate or the aqueous acids which reaches and contains a chlorination salt, and being obtained.

[Claim 2] In the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, primary blackening of the front face of a copper plate is carried out in the aqueous acids containing a selenium. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or the copper plate of the copper rust colored spot point pattern characterized by spraying the aqueous acids which reach and contain a chlorination salt on the front face of the copper plate concerned, and being obtained.

[Claim 3] In the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, primary blackening of the front face of a copper plate is carried out in the aqueous acids containing a selenium. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or the copper plate of the copper rust colored spot point pattern characterized by the front face of the copper plate concerned and being obtained in the PATTENGU member to which the aqueous acids which reach and contain a chlorination salt were made to sink in or adhere.

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[Translation done.]

*green surface coloration = verdigris = patina*

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the copper plate which made the copper rust colored spot point pattern form in the front face of copper or a copper alloy plate chemically, and its art.

[0002]

[Description of the Prior Art] It is known widely that the precise copper rust coat by which poor solubility was stabilized in water by prolonged contact for the atmospheric-air component which contains moisture on the surface of copper will be obtained. Various examination of acquiring a copper rust colored spot point pattern from such a copper rust color appearance having the sophisticated-design effectiveness simply artificially is carried out.

[0003] For example, the conventional artificial copper rust approach holds what carried out the chemical treatment to the copper front face by the heat-and-high-humidity environment. However, by such approach, there was also a problem which will deform if forming only the processor which holds a tabular big product by such environment itself applies heat to tabular copper or a tabular copper alloy plate difficult.

[0004] Moreover, although the approach of carrying out paint of the different color tone and different shade on it to the substrate pattern which performed copper rust color paint, and forming a copper rust colored spot point pattern was proposed, the adhesion of a paint film was bad and it was difficult for a problem to have been in endurance and to have made the copper rust color of the nature also in appearance resemble.

[0005]

[Problem(s) to be Solved by the Invention] In view of the above technical problems, that a heat strain and heat deformation should be prevent to large-sized and thin copper or a copper alloy plate, this invention can perform coloring processing easily chemically in ordinary temperature, be excellent in the adhesion and endurance of a coloring coat, and aim at formation of a copper rust colored spot point pattern with the high-class feeling near a natural copper rust color, and offer of a copper plate obtained by make it such.

[0006]

[Means for Solving the Problem] Invention according to claim 1 processed the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, and it considered as the copper plate of the copper rust colored spot point pattern characterized by the carbonate or being processed and obtained in the aqueous acids which reach and contain a chlorination salt after that.

[0007] in order for the aqueous acids which contain a selenium here to mean the water solution of the oxidizing quality contained 0.3 - 3% of selenious acids, to melt and prepare a selenium dioxide etc. in water and to stabilize blackening of the front face of a copper plate -- a copper sulfate -- 0.1 - 3% -- or -- and you may add 0.1 - 1% of sulfuration salts. A front face will be colored a black system if a copper plate etc. is immersed in the aqueous acids (henceforth a black-oxide-finish water solution) containing

such a selenium. It rinsed after that and the front face was dried.

[0008] Moreover, especially if it says a carbonate or that the aqueous acids which reach and contain a chlorination salt contain salts, such as an ammonium carbonate and an ammonium chloride, it reacts with a black coat and basic copper salt is formed, it will not be limited, but it reaches and a carbonate or the thing which melted the chlorination salt ten to 50 g/l, respectively is said to the water solution which diluted the aqueous acids containing the selenium for the above-mentioned black oxide finish 10 to 20 times with water. It reaches, and if surface treatment is carried out in such a carbonate or the aqueous acids (henceforth a copper rust water solution) containing a chlorination salt, a copper rust love scene will be formed on the surface of a copper plate.

[0009] Invention according to claim 2 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it reached and considered as the copper plate of the copper rust colored spot point pattern characterized by spraying the aqueous acids containing a chlorination salt on the front face of the copper plate concerned, and being obtained. Although a copper rust colored spot point pattern can be formed also by the approach according to claim 1, the \*\*\*\*\* of a coloring coat is ensured, and in order to make the copper rust colored spot point pattern which has a high-class feeling more form, invention according to claim 2 is made.

[0010] Preliminary washing of the front faces, such as a copper plate, was carried out in the dilution sulfuric-acid water solution etc., primary blackening was carried out in the black-oxide-finish water solution after rinsing, substrate copper rust processing was carried out in the copper rust water solution after rinsing desiccation, pickling was carried out in the dilution sulfuric-acid water solution after desiccation and rinsing, secondary blackening was carried out after rinsing, the copper rust water solution was used for the front face for the spray gun for paint etc. after rinsing and desiccation, and the spray was carried out. Then, while the waterdrop by which the spray was carried out reacts to a front face partially, since it dries, a copper rust colored spot point pattern is formed. Therefore, if it repeats twice or more, taking a desiccation process for a copper rust water solution if needed, the copper rust colored spot point pattern more near nature will be formed.

[0011] Invention according to claim 3 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it considered as the copper plate of the copper rust colored spot point pattern characterized by the front face of the copper plate concerned and being obtained in the PATTENGU member to which the aqueous acids which reach and contain a chlorination salt were made to sink in or adhere. PATTENGU [ this ] so that a front face might be lightly struck using the PATTENGU member which instead absorbs copper rust water solutions, such as cloth and sponge, in addition to the process which carries out the spray of the copper rust water solution in invention according to claim 2. When done in this way, the remains of PATTENGU carried out an appearance like \*\*\*\* produced naturally the degree.

[0012] Thus, after making a copper rust colored spot point pattern form on the surface of a copper plate, it finished by carrying out clear paint.

[0013]

[Embodiment of the Invention] The gestalt of desirable operation of this invention is explained hereafter. the black-oxide-finish water solution which pickled the copper plate of the thin shape of a sheet with a thickness of 0.1-0.4mm for about 1 minute in the dilution sulfuric-acid water solution 1 to 5%, and diluted 3% of selenic-acid water solution about 4 times after rinsing -- ordinary temperature -- primary blackening during about 5 - 6 minutes was carried out. Then, it rinsed and dried, and water was

immersed in about 100ml of black-oxide-finish water solutions of the same concentration as the above at about 1000ml, in addition the copper rust water solution which diluted, and melted and prepared 20g of ammonium carbonates, and 30g of ammonium chlorides, and substrate copper rust processing was carried out. Next, rinsing preliminary washing was carried out after desiccation, acid cleaning was carried out in the dilution sulfuric-acid water solution, and secondary blackening was performed for about 10 minutes after rinsing. The spray of the copper rust water solution prepared to the concentration same with having used for the above-mentioned substrate copper rust on the front face rinsed and dried after this blackening was carried out. After the copper rust water solution which carried out the spray to the 1st time dried, when it was made to dry by carrying out the 2nd spray, the copper rust spot pattern that a mimetic diagram was shown in drawing 1 was formed again.

[0014] The 1st above-mentioned spray was carried out similarly, carried out the 2nd spray using the old liquid which carried out copper rust processing last time, and it wiped off so that it might strike using a cloth towel etc. Thereby, the copper rust pattern as shown in drawing 2 was formed. Moreover, when it wiped off so that copper rust processing of after that still older liquid might be included in a PATTENGU member and might be struck strongly, a pattern that the copper rust part as shown in drawing 3 became thin was formed.

[0015]

[Effect of the Invention] According to the copper rust colored spot point encaustic formation approach by the chemical preparation concerning this invention, since it can process in ordinary temperature, there is no heat deformation, and not only heavy-gage ingredients, such as a casting used as a copper base material like before, but the copper plate of the shape of a thin sheet etc. can be processed easily.

Moreover, after carrying out primary black oxide finish and substrate copper rust processing, secondary black oxide finish is carried out, and if copper rust color processing is carried out, the adhesion to the copper plate of chemical conversion coatings will become what was very excellent.

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EFFECT OF THE INVENTION

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[Effect of the Invention] According to the copper rust colored spot point encaustic formation approach by the chemical preparation concerning this invention, since it can process in ordinary temperature, there is no heat deformation, and not only heavy-gage ingredients, such as a casting used as a copper base material like before, but the copper plate of the shape of a thin sheet etc. can be processed easily. Moreover, after carrying out primary black oxide finish and substrate copper rust processing, secondary black oxide finish is carried out, and if copper rust color processing is carried out, the adhesion to the copper plate of chemical conversion coatings will become what was very excellent.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] In view of the above technical problems , that a heat strain and heat deformation should be prevent to large-sized and thin copper or a copper alloy plate , this invention can perform coloring processing easily chemically in ordinary temperature , be excellent in the adhesion and endurance of a coloring coat , and aim at formation of a copper rust colored spot point pattern with the high-class feeling near a natural copper rust color , and offer of a copper plate obtained by make it such .

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MEANS

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[Means for Solving the Problem] Invention according to claim 1 processed the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, and it considered as the copper plate of the copper rust colored spot point pattern characterized by the carbonate or being processed and obtained in the aqueous acids which reach and contain a chlorination salt after that.

[0007] in order for the aqueous acids which contain a selenium here to mean the water solution of the oxidizing quality contained 0.3 - 3% of selenious acids, to melt and prepare a selenium dioxide etc. in water and to stabilize blackening of the front face of a copper plate -- a copper sulfate -- 0.1 - 3% -- or -- and you may add 0.1 - 1% of sulfuration salts. A front face will be colored a black system if a copper plate etc. is immersed in the aqueous acids (henceforth a black-oxide-finish water solution) containing such a selenium. It rinsed after that and the front face was dried.

[0008] Moreover, especially if it says a carbonate or that the aqueous acids which reach and contain a chlorination salt contain salts, such as an ammonium carbonate and an ammonium chloride, it reacts with a black coat and basic copper salt is formed, it will not be limited, but it reaches and a carbonate or the thing which melted the chlorination salt ten to 50 g/l, respectively is said to the water solution which diluted the aqueous acids containing the selenium for the above-mentioned black oxide finish 10 to 20 times with water. It reaches, and if surface treatment is carried out in such a carbonate or the aqueous acids (henceforth a copper rust water solution) containing a chlorination salt, a copper rust love scene will be formed on the surface of a copper plate.

[0009] Invention according to claim 2 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it reached and considered as the copper plate of the copper rust colored spot point pattern characterized by spraying the aqueous acids containing a chlorination salt on the front face of the copper plate concerned, and being obtained. Although a copper rust colored spot point pattern can be formed also by the approach according to claim 1, the \*\*\*\*\* of a coloring coat is ensured, and in order to make the copper rust colored spot point pattern which has a high-class feeling more form, invention according to claim 2 is made.

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twice or more, taking a desiccation process for a copper rust water solution if needed, the copper rust colored spot point pattern more near nature will be formed.

[0011] Invention according to claim 3 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it considered as the copper plate of the copper rust colored spot point pattern characterized by the front face of the copper plate concerned and being obtained in the PATTENGU member to which the aqueous acids which reach and contain a chlorination salt were made to sink in or adhere. PATTENGU [ this ] so that a front face might be lightly struck using the PATTENGU member which instead absorbs copper rust water solutions, such as cloth and sponge, in addition to the process which carries out the spray of the copper rust water solution in invention according to claim 2. When done in this way, the remains of PATTENGU carried out an appearance like \*\*\*\* produced naturally the degree.

[0012] Thus, after making a copper rust colored spot point pattern form on the surface of a copper plate, it finished by carrying out clear paint.

[0013]

[Embodiment of the Invention] The gestalt of desirable operation of this invention is explained hereafter. the black-oxide-finish water solution which pickled the copper plate of the thin shape of a sheet with a thickness of 0.1-0.4mm for about 1 minute in the dilution sulfuric-acid water solution 1 to 5%, and diluted 3% of selenic-acid water solution about 4 times after rinsing -- ordinary temperature -- primary blackening during about 5 - 6 minutes was carried out. Then, it rinsed and dried, and water was immersed in about 100ml of black-oxide-finish water solutions of the same concentration as the above at about 1000ml, in addition the copper rust water solution which diluted, and melted and prepared 20g of ammonium carbonates, and 30g of ammonium chlorides, and substrate copper rust processing was carried out. Next, rinsing preliminary washing was carried out after desiccation, acid cleaning was carried out in the dilution sulfuric-acid water solution, and secondary blackening was performed for about 10 minutes after rinsing. The spray of the copper rust water solution prepared to the concentration same with having used for the above-mentioned substrate copper rust on the front face rinsed and dried after this blackening was carried out. After the copper rust water solution which carried out the spray to the 1st time dried, when it was made to dry by carrying out the 2nd spray, the copper rust spot pattern that a mimetic diagram was shown in drawing 1 was formed again.

[0014] The 1st above-mentioned spray was carried out similarly, carried out the 2nd spray using the old liquid which carried out copper rust processing last time, and it wiped off so that it might strike using a cloth towel etc. Thereby, the copper rust pattern as shown in drawing 2 was formed. Moreover, when it wiped off so that copper rust processing of after that still older liquid might be included in a PATTENGU member and might be struck strongly, a pattern that the copper rust part as shown in drawing 3 became thin was formed.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The example in the condition of having formed the spot pattern by the spray is shown.

[Drawing 2] The example in the condition of having formed the spot pattern in PATTENGU is shown.

[Drawing 3] The example in the condition of having formed the spot pattern in strong PATTENGU is shown.

[Description of Notations]

1 A Part for Copper Rust Color Part

2 Part of Blackish Color Tone

3 Part of Color Tone of Tea System

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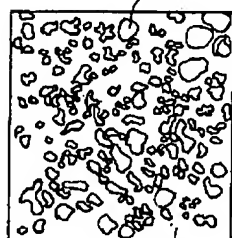
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DRAWINGS

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[Drawing 1]



2

[Drawing 2]



2

[Drawing 3]



3

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[Translation done.]



## 【特許請求の範囲】

【請求項1】銅板の表面に化学的に緑青色斑点模様を形成する着色方法において、銅板の表面をセレンを含有する酸性水溶液にて処理し、その後に炭酸塩又は、及び、塩化塩を含有する酸性水溶液にて処理して得られることを特徴とする緑青色斑点模様の銅板。

【請求項2】銅板の表面に化学的に緑青色斑点模様を形成する着色方法において、銅板の表面をセレンを含有する酸性水溶液にて1次黒染処理し、炭酸塩又は、及び、塩化塩を含有する酸性水溶液にて下地緑青処理し、その後10に酸洗浄し、当該セレンを含有する酸性水溶液にて2次黒染処理し、その後に炭酸塩又は、及び、塩化塩を含有する酸性水溶液を当該銅板の表面に噴霧して得られることを特徴とする緑青色斑点模様の銅板。

【請求項3】銅板の表面に化学的に緑青色斑点模様を形成する着色方法において、銅板の表面をセレンを含有する酸性水溶液にて1次黒染処理し、炭酸塩又は、及び、塩化塩を含有する酸性水溶液にて下地緑青処理し、その後10に酸洗浄し、当該セレンを含有する酸性水溶液にて2次黒染処理し、その後に炭酸塩又は、及び、塩化塩を含有する酸性水溶液を浸漬又は付着させたパッテング部材にて当該銅板の表面をパッテングして得られることを特徴とする緑青色斑点模様の銅板。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は銅又は銅合金板の表面に化学的に緑青色斑点模様を形成させた銅板及びその処理方法に関する。

## 【0002】

【従来の技術】銅の表面に水分を含む大気成分との長期間の接触により水に難溶性の安定した緻密な緑青被膜が得られることは広く知られている。このような緑青色外観は優れたデザイン効果を有することから人工的に簡単に緑青色斑点模様を得ることが各種検討されている。

【0003】例えば、従来の人工緑青方法は銅表面に薬品処理したものを高温多湿環境に保持するものである。しかし、このような方法では大きな板状の製品をそのような環境に保持するだけの処理装置を設けること自体が困難であり、また板状の銅又は銅合金板に熱を加えると変形してしまう問題もあった。

【0004】また、緑青色塗装を施した下地模様に、その上に異なる色調や濃淡の塗装をして緑青色斑点模様を形成する方法が提案されているが、塗膜の密着性が悪く、耐久性に問題があり、外観的にも天然の緑青色に近似させることは困難であった。

## 【0005】

【発明が解決しようとする課題】本発明は上記のような課題に鑑みて、大型で薄い銅又は銅合金板に対して熱ひずみや熱変形を防止すべく常温において、化学的に容易に着色処理が出来、着色皮膜の密着性及び耐久性に優

れ、天然緑青色に近い高級感のある緑青色斑点模様の形成及び、そのようにして得られた銅板の提供を目的とする。

## 【0006】

【課題を解決するための手段】請求項1記載の発明は銅板の表面に化学的に緑青色斑点模様を形成する着色方法において、銅板の表面をセレンを含有する酸性水溶液にて処理し、その後に炭酸塩又は、及び、塩化塩を含有する酸性水溶液にて処理して得られることを特徴とする緑青色斑点模様の銅板とした。

【0007】ここでセレンを含有する酸性水溶液とは亜セレン酸0.3～3%含有する酸化性的水溶液をいい、二酸化セレン等を水に溶かして調合してもよく銅板の表面の黒染めを安定させるために硫酸銅を0.1～3%又は、及び、硫化塩0.1～1%添加してもよい。このようなセレンを含有する酸性水溶液（以下黒染水溶液という）に銅板等を浸漬すると表面が黒色系に着色される。その後10に水洗し、表面を乾燥させた。

【0008】また、炭酸塩又は、及び、塩化塩を含有する酸性水溶液とは例えば、炭酸アンモニウム、塩化アンモニウム等の塩を含有することをいい、黒色皮膜と反応して塩基性銅塩を形成するものならば特に限定されず、上記黒染用のセレンを含有する酸性水溶液を水で10～20倍に希釈した水溶液に炭酸塩又は、及び、塩化塩をそれぞれ10～50g/l溶かしたものをいう。このような炭酸塩又は、及び、塩化塩を含有する酸性水溶液（以下緑青水溶液という）にて表面処理すると銅板の表面に緑青色模様が形成される。

【0009】請求項2記載の発明は、銅板の表面に化学的に緑青色斑点模様を形成する着色方法において、銅板の表面をセレンを含有する酸性水溶液にて1次黒染処理し、炭酸塩又は、及び、塩化塩を含有する酸性水溶液にて下地緑青処理し、その後10に酸洗浄し、当該セレンを含有する酸性水溶液にて2次黒染処理し、その後に炭酸塩又は、及び、塩化塩を含有する酸性水溶液を当該銅板の表面に噴霧して得られることを特徴とする緑青色斑点模様の銅板とした。請求項1記載の方法にても緑青色斑点模様を形成することはできるが、着色皮膜の安着性を確実にし、より高級感のある緑青色斑点模様を形成させるために請求項2記載の発明がなされたものである。

【0010】銅板等の表面を希釈硫酸水溶液等で予備洗浄し、水洗後に黒染水溶液にて1次黒染処理し、水洗乾燥後に緑青水溶液にて下地緑青処理し、乾燥、水洗後に希釈硫酸水溶液にて酸洗いをし、水洗後に2次黒染処理し、水洗、乾燥後に緑青水溶液を表面に塗装用スプレーガン等を用いてスプレーした。その後、表面にスプレーされた水滴が部分的に反応しながら、乾燥されてくるので緑青色斑点模様が形成される。従って、必要に応じて緑青水溶液を乾燥工程をとりながら2回以上繰り返すとより天然に近い緑青色斑点模様が形成される。

青に用いたのと同様の濃度に調合した緑青水溶液をスプレーした。1回目にスプレーした緑青水溶液が乾燥した後に再度、2回目のスプレーをして乾燥させると、図1に模式図を示すような緑青斑点模様が形成された。

【0014】上記の1回目のスプレーまでは同様に実施し、前回緑青処理した古い液を用いて2回目のスプレーを実施し、布タオル等を用いてたたくようにふきとった。これにより、図2に示すような緑青模様が形成された。またその後、さらに古い液の緑青処理をパッティング部材に含ませて強くたたくようにふきとると図3に示すような緑青部分が薄くなった模様が形成された。

【発明の効果】本発明に係る化学的処理による緑青色斑点模様形成方法によれば、常温で処理出来るので熱変形が無く、従来のような銅基材とする鋳物等の厚肉材料のみならず薄いシート状の銅板等も容易に処理出来る。また1次黒染、下地緑青処理をした後に2次黒染して緑青色処理すると化学皮膜の銅板への密着性が非常に優れたものとなる。

【図1】スプレーにて斑点模様を形成した状態の例を示す。

【図2】パッテングにて斑点模様を形成した状態の例を示す。

【図3】強いパッテングにて斑点模様を形成した状態の例を示す。

【符号の説明】

- 1 緑青色部分
- 2 黒っぽい色調の部分
- 3 茶系の色調の部分

【0012】このようにして銅板の表面に緑青色斑点模様を形成させた後にクリア塗装をして仕上げた。

【0013】

【発明の実施の形態】本発明の望ましい実施の形態を以下、説明する。厚み0.1～0.4mmの薄いシート状の銅板を1～5%希釈硫酸水溶液にて約1分間、酸洗いし、水洗後に、3%のセレン酸水溶液を約4倍に希釈した黒染水溶液にて常温、約5～6分間1次黒染処理した。その後、水洗、乾燥し、上記と同様の濃度の黒染水溶液約100mlに水を約1000ml加えて、希釈し、炭酸アンモニウム20g及び塩化アンモニウム30gを溶かして調合した緑青水溶液に浸漬して下地緑青処理した。次に乾燥後に水洗予備洗浄し、希釈硫酸水溶液にて酸洗浄し、水洗後、2次黒染処理を約10分間施した。この黒染処理後水洗、乾燥させた表面上記下地緑

【图3】

